
Chapter 7

Kiln Dust

Disposal of Wastes from Cement Production

1. INTRODUCTION	237
2. REGULATORY ASPECTS OF DUMPING SOLID WASTE MATERIALS.....	238
2.1 Swiss TVA 95	238
2.2 E.P.A.'s TCLP Leaching Test	242
2.3 European DIN 38 405 D24 Leaching Test	243
3. DISPOSAL OF General CEMENT PLANT WASTES.....	243
4. DISPOSAL OF KILN DUSTs.....	246
4.1 Discarded Dust, its Potential and Drawbacks	246
4.2 Methods of In-Plant Disposal of Untreated Kiln Dust	248
4.2.1 Addition of Dust to Cement	248
4.2.2 Returning to Kiln after Granulation or Compaction.....	249
4.3 Methods for In-Plant Use of Kiln Dust after Removal of Alkalis	252
4.3.1 Removal by Simple Leaching.....	252
4.3.2 Removal by Passamaquoddy Technology Recovery Scrubber	255
4.3.3 Removal by Auxiliary Kiln or by Fuller Fluidised Bed Reactor	256
4.4 Reported Plant External Uses of Kiln Dust	258
4.4.1 As Fertilizer.....	258
4.4.2 As Raw Material for Artificial (N-Viro) Soil	260
4.4.3 As Asphalt Filler	262
5. Disposal of Bypass Dust.....	263
5.1 In Plant Use.....	263
6. DISPOSAL OF REFRACTORIES.....	265
6.1 Background	265
6.2 Materials Involved and their Chemical Compositions.....	265
6.2.1 Materials Involved	265
6.2.2 Chemical Composition	266
6.3 Regulatory Aspects / Manufacturers Safety Data Sheets	267
6.4 In-plant refractories disposal	267
6.4.1 Plant "A".....	267
6.4.2 Plant "B".....	267
7. Recycling of spent cement kiln refractories.....	268

8. Appendixes.....	270
8.1 Appendix Ia.....	270
8.2 Appendix Ib.....	271
8.3 Appendix Ic.....	272
8.4 Appendix Ib.....	273

1. INTRODUCTION

Whereas natural processes generally occur in cycles, in which the waste products created do not harm the biosphere, the same cannot be said for human activities at today's high population densities. The cement industry is no exception in that it generates wastes whose properties range from being an unsightly nuisance to being definitely toxic. Table 1 lists these principal solid, liquid and gaseous wastes. Whereas the gaseous wastes go into the atmosphere and rapidly lose their identity by dilution, the same is not true for solid types. The latter remain in possession of the plant, which has the responsibility for their safe disposal

Table 1: Wastes generated in Cement Plants

Solid Wastes

- ◆ overburden, earth
- ◆ kiln dust, bypass dust
- ◆ mill dust
- ◆ sulphur absorbent
- ◆ reject production
- ◆ used refractories
- ◆ cleaning dust
- ◆ scrap iron
- ◆ rubber wastes (tyres, belts)
- ◆ test prisms / cubes

Liquid Wastes

- ◆ rainwater / wash water
- ◆ sewage water
- ◆ oils / greases / emulsions
- ◆ laboratory chemicals
- ◆ solvents

Gaseous Wastes

- ◆ CO₂, NO_x, SO₂, Hydrocarbons, etc.

In the present article the main emphasis will be placed on the management of the large tonnage wastes namely refractory tear out and the various types of kiln dusts. No mention will be given to that waste generated in the largest quantities, namely CO₂ emissions, of which the cement industry is a significant but not the major contributor.

2. REGULATORY ASPECTS OF DUMPING SOLID WASTE MATERIALS

In the past most manufacturing and processing industries simply dumped their waste materials, euphemistically calling them "landfill". They did this because it made economic sense and an awareness of the accompanying burden to the environment existed in only rare cases, if at all.

Today the situation has changed. Environmental awareness is only all too present and those harmlessly dumped wastes of yester year are now becoming the potential environmental time-bombs of today and tomorrow. Many a cement plant is going to be confronted with a bill for cleaning up its dumped materials, costs which will certainly be a multiple of the sum originally "saved". No cement company in a developed country is today going to be allowed to wind up its operations until it has made certain that all the materials it dumped during its operational lifetime are in a form which poses no threat to the environment.

Some examples of the regulations applicable to the dumping of materials will now be given.

2.1 Swiss TVA 95

The Swiss TVA regulation of December 1990 is a typical example applicable to the dumping of all types of material. It defines three categories of dumping operations, namely of the "inert material", "residual material" and of the "reactor" types. Details of the requirements for end storage in inert and residual dumps are given in Tables 2, 3 and 4. The use of reactor dumps is presently reserved for slag from rubbish incinerating plants and for sewage sludge (< 65 % H₂O), inert/building waste materials, etc. when no capacity is available in inert or residual material dumps. Dumps for highly toxic materials do not exist and such materials have to be eliminated by other means.

Table 2: Swiss Dumping Regulations (TVA-1990)
Compositional Requirements

MT-Mat. No	TVA Requirements	
Material	for End Storage	
Condition	Inert	Residual
Composition known (%)		> 95
Stone like Material (%)	> 95	
H ₂ O-soluble substances (%)	0,5	5
Organic material (% C)		5
Pb (ppm)	500	
Cd (ppm)	10	
Cu (ppm)	500	
Ni (ppm)	500	
Hg (ppm)	2	
Zn (ppm)	1000	
Lipo. org. Cl compods. (ppm)		10
Gas formation with H ₂ O		none
Reaction with self, H ₂ O, air		none
Neutral, Capacity (Mol/kg)		1

The following building material can be included in an inert substance deposit:
concrete, tiles, asbestos cement, class masonry and road construction wastes.

Table 3: Elutriation Test (No. 1)
Requirements in Swiss Dumping Regulations (TVA 1990)
(Elutriation in CO₂ Saturated Solution)

MT-Mat. No	TVA Requirements (mg/l)	
Material	for End Storage	
Condition	Inert	Residual
Al	1.000	10.00
As	0.001	0.10
Ba	0.50	5.00
Pb	0.10	1.00
Cd	0.01	0.10
Cr-III	0.05	2.00
Cr-VI	0.01	0.10
Co	0.05	0.05
Cu	0.20	0.05
Ni	0.20	2.00
Hg	0.005	0.01
Zn	0.50	5.00
Sn	0.20	2.00

Materials which may be deposited in inert substance dumps can either be unreactive substances as defined in the mentioned tables or "building wastes" such as concrete, tiles, asbestos cement products, glass and masonry/road construction wastes. Materials such as metal, paper, wood, and textiles must be removed from "building wastes" as much as is economically practical.

As can be seen in the Tables 4 to 6 there are limits set down on the chemical composition (toxic metals, organic substances) of the materials themselves and on their leaching behaviour in two elutriation tests. In the first test CO₂ is bubbled through the solution to keep the pH value low and thus ensure that the toxic cations are brought into solution and not precipitated. In the second elutriation test, in which the anions and organic substances present are determined, distilled water without CO₂ is employed.

Table 4: Elutriation Test (No. 2)
Requirements in Swiss Dumping Regulations (TVA 1990)
(Elutriation in Distilled Water)

MT-Mat. No	TVA Requirements (mg/l)	
Material	for End Storage	
Condition	Inert	Residual
NH ⁴⁺ / NH ₃	0.50	5.00
TI	not specified	not specified
Cyanide	0.01	0.10
Fluoride	1.00	10.00
Nitrite	0.10	1.00
Sulphite	0.10	1.00
Sulphide	0.01	0.10
Phosphate	1.00	10.00
DOC *	20.00	50.00
HC's	0.50	5.00
LOC *	0.01	0.05
Cl Sol *	0.01	0.10
pH Value	6 - 12	6 - 12

DOC: dissolved organic carbon

HC: hydrocarbons

LOC: lypophilic organic chlorine compounds

Cl Sol: chlorinated solvents

As a result of these regulations the following restrictions prevent (in Switzerland) the dumping of waste materials such as kiln dust and refractories:

- ◆ H₂O soluble substances < 0.5 %, resp < 5.0 % exceeded due to presence of soluble alkali chlorides and sulphates
- ◆ total Pb and Zn levels over 500 ppm due to use of alternative fuels and raw material components
- ◆ soluble Pb and Zn limits exceeded due to use of alternative fuels and raw material components.
- ◆ soluble Cr⁶⁺ limit exceeded in the case of spent magnesia-chrome refractories

2.2 E.P.A.'s TCLP Leaching Test

In the USA the disposal of kiln dust and of spent kiln refractories is mainly by dumping the refractories, often in plant external sites. This disposal is regulated by the Resources Conservation and Recovery Act (RCRA) and hence the class of dump to which they can be sent, is decided by their behaviour according to the Toxicity Concentration Leaching Procedure (TCLP) test. Details of the latter and the limits defined for the various elements in the leachate are given in Table 5.

Table 5: Details of USEPA's TCLP Leaching Test

Leaching Medium	Demineralised H ₂ O	Element	Extract Limit (mg/l)
	+ acetic acid (pH=5)	Ag	5
Liquid / Solid ratio	20 : 1	As	5
Max. Particle Size (mm)	9.5	B	
Nr. of Extractions	1 (agitation)	Ba	100
Extraction Time (hr)	18 ± 2	Be	0.007
		Cd	1
		Cr	5
		Cu	
		CrHg	0.2
		Ni	70
		Pb	5
		Se	1
		Sb	1
		Tl	7
		Zn	

As can be seen the elements defined are (with one exception) trace toxic elements and as such only present in natural raw materials and in new, unused refractories in trace quantities, if at all. Trace quantities can, however, be picked up during their presence in the kiln. The main oxides from which kiln refractories are produced i.e. SiO₂, Al₂O₃, CaO, MgO and the trace oxides Fe₂O₃, K₂O, Na₂O etc. are not stipulated and are anyway the same oxides as found in PC clinker.

The one exception is Cr which, as Cr₂O₃, is a major oxide component of magnesia chrome refractories, with some refractories containing up to almost 18 %. Although it is wholly present as insoluble Cr₂O₃ in the new, unused bricks this is partially converted to a soluble alkali sulphate chromate during kiln operations and therefore contains soluble Cr⁶⁺. On the basis of tests carried out at HMC Corporate Services up to 0.4 % of soluble Cr⁶⁺ has been determined in spent magnesia chrome bricks which originally contained 17 % Cr₂O₃.

Spent magnesia-chrome bricks are therefore not likely to pass the TCLP test for disposal in a municipal garbage dump and hence will have to be treated before such a disposal with ensuing costs. A change to refractories of the chrome-ore free magnesia-spinel or doloma types avoids this disposal problem completely.

2.3 European DIN 38 405 D24 Leaching Test

According to this regulation the following concentrations of Cr^{6+} dictate the disposal of all wastes, but especially those containing chromite ore (magnesia chrome bricks) as follows:

- ◆ < 0.1mg/l: in household garbage dump
- ◆ > 0.1 mg/l < 0.5 mg/l: in toxic material dump
- ◆ >0.5 mg/l: special treatment or must be dumped underground

3. DISPOSAL OF GENERAL CEMENT PLANT WASTES

Of the general wastes generated in cement plants examples of their management at the Rekingen and Ciminias plants are listed in Tables 6 and 7. Whereas the procedures for dealing with wastes are already established in developed countries, plants in developing countries invariably have to set up their own infrastructure. It is important that clearly marked collection centres are located near to the places the wastes are generated and that their use is promoted.

Table 6: Waste Concept at Rekingen

Material	Quantity per Month	Internal Disposal	External Disposal
Office, stores			
Paper carton		Kiln	
Workshop			
Ferrous	4t		Scap metal
Non-ferrous	2t		Scap metal
Rags			Garbage incinerator
Waste Wood Plant			
Ferrous	40t		Scrap metal
Non-ferrous	3t		Scrap metal
Masonry	60t	Mix bed	
Paper, styropor	0.5t		Garbage incinerator
Water		Mix bed	
Refractories			
Cuttings	10	Mix bed	
Tear out	500 t/a	Mid bed	
Garage			
Tyres	0.5t	Siggenthal	
Oil / Air filters	50 kg	Siggenthal	
Waste Oil	1000l		Waste oil dealer
Laboratory			
Liquid waste	10l		Special collection
Solid waste	10l		Special collection
Radioactive source			Supplier
Various			
Glass			Local collection
Light tubes	100		Special Collectio

Table 7: Waste to be Disposed at Ciminias Plant

Material	Means of Disposal
	Internal & External use
Absorbed Diesel Spillage	Used as combustable
Filter bags	Reused, sold for reuse
	Internal use
Asbestos components	Crushed, added to raw mill
Cement ex spillage's	Returned ro process
Clinical wastes	Incinerated in containers
Glass	Crushed, added to raw mill
Lamps	Added to raw mill
Rags / cloths	Incinerated in containers
Refractories (Cr containing)	Crushed, added to raw mill
Wastes from charcoal	Added to raw mill via clay
Sax ex sand blasting	Added to raw mill
	External use
Askarel oil	Incinerated externally
Clothes / shoes / helmets	Sold for recycling
Concrete cubes	Given to personnel
Fibre glass	Sold for recycling
Filter elements	Pressed and sold
Iron ex slag	Sold to foundries
Metal / electrical scrap	Sold for recycling
Oils / greases	Sold for recycling
Paper ex office	Sold for recycling
Plastics	Sold for recycling
Refractories	Sold for reuse
Rubber / car batteries	Sold for recycling

It is the disposal of the larger quantities of cement plant specific wastes kiln dust (up to 300'000 tpa at one Group plant) and spent refractories (up 800 tons at some Group plants) that must receive the greatest attention. Whereas refractories are consumable items and it is understandable that there will be remnants to be disposed of, this is not the case with kiln dusts. In fact most Group plants do not have to discard dust and those actually doing so are forced to do so for several reasons:

- ◆ production in wet kilns of low(er) alkali cements from raw materials which do not have sufficiently low alkali levels to produce such cements without the discarding of dust
- ◆ use of a bypass in dry process kilns when the raw materials have a too high Cl content
- ◆ to prevent the formation of rings in wet process kilns caused by a molar excess of SO₃ over alkalis.

Most of the dust discarded in the Group is generated at wet plants in the USA and Canada for the production of low alkali cements and thus in countries whose standard specifications still do not allow the incorporation of kiln dust into cement.

4. DISPOSAL OF KILN DUSTS

4.1 Discarded Dust, its Potential and Drawbacks

The total quantity of dust discarded annually in the "Holderbank" Group amounts to some 1.8 mio. tpa, with the quantity per plant ranging from zero (most cases) to over 200'000 tpa at a few N. American plants. In these latter cases the kiln feed / clinker factor can be as high as 1.91 which means having to process excessive quantities of kiln feed and a faster depletion of the reserves.

The chemical composition of the discarded kiln and bypass dust varies with kiln type as well as from plant to plant. Details main oxide composition of kiln dust discarded at Group Plants is given in Table 8, with details of the heavy metal levels in American kiln dusts being listed in Table 9.

Table 8: Analyses of Dusts from Various Kiln Types

Kiln type	Suspension preheater				Grate preheater		Wet long		Dry long	
	Filter		By-pass		(Lepol)					
Abbreviation	DS-F		DS-BP		DG		WL		DL	
Number of samples	19		6		13		36		2	
	from-to	average	from-to	average	from-to	average	from-to	average	from-to	average
L.o.I	31.3-37.9	34.5	4.3-13.3	8.9	5.2-28.6	15.6	3.8-33.8	22.6	21.8-27.0	24.4
SiO ₂	9.0-16.8	13.1	13.1-16.4	14.4	4.9-21.0	14.0	3.5-18.3	13.3	7.6-11.3	9.5
Al ₂ O ₃	2.2-6.6	4.1	3.0-4.5	3.7	1.1-9.0	3.7	1.4-6.9	3.9	1.6-3.1	2.9
Fe ₂ O ₃	1.2-3.3	2.2	1.2-2.5	1.7	0.4-3.7	1.5	0.6-4.3	1.9	1.1-1.7	1.4
CaO	38.6-45.7	42.2	44.4-60.8	52.3	14.9-52.7	36.1	10.6-53.8	41.7	31.7-49.6	40.2
MgO	0.70-2.4	1.4	0.80-2.7	1.7	0.4-2.6	1.0	0.3-4.5	1.3	1.3-1.3	1.3
SO ₃	0.04-2.4	0.75	2.6-4.8	3.6	1.3-32.2	121.1	0.68-36.7	6.3	6.0-14.8	10.4
K ₂ O	0.35-2.7	1.07	4.1-12.6	8.8	3.4-35.2	13.2	0.79-38.1	6.0	0.88-15.8	8.3
Na ₂ O	0.07-0.30	0.17	0.17-1.6	0.62	0.18-2.6	1.1	0.12-14.1	1.3	0.07-1.3	0.69
Cl	0.04-0.68	0.25	2.3-7.1	4.2	0.10-2.0	0.81	0.07-10.8	1.3	0.88-1.3	0.69
Free lime	0.00-0.54	0.12	2.6-31.1	4.2	0.71-7.7	6.32	0-17.9	6.33	1.3-8.8	5.1

Table 9: Total (acid soluble) metals in cement and cement kiln dust

		Total In Cement, mg/kg				Total In CKD, mg/kg				Ratio of Avg. Cement /CKD
		Min.	Avg.	Max.	No.	Min.	Avg.	Max.	No.	
Volatile ↑ ↓ Refractory	Mercury	<0.001	0.014	0.039	21	0.004	0.660	25.500	68	2%
	Selenium	0.62	NM	2.23	6	2.68	28.14	307.00	54	NM
	Thallium	0.01	1.08	2.68	32	1.40	43.24	776.00	89	2%
	Cadmium	0.03	0.34	1.12	42	0.1	10.3	59.6	81	3%
	Lead	1	12	75	82	34	434	7390	95	3%
	Antimony	0.7	NM	4.0	2	0.3	NM	3.4	9	NM
	Silver	6.75	9.20	19.90	93	4.8	10.53	40.70	92	87%
	Arsenic	5	19	71	54	2	18	159	50	106%
	Nickel	10	31	129	85	1	22	60	65	141%
	Barium	91	280	1402	94	35	172	767	95	163%
	Beryllium	0.32	1.13	305	93	0.13	0.65	3.54	94	174%
	Chromium	25	76	422	94	8	41	293	95	185%

Notes:

- 1) Exclude non-detectable values
- 2) NM indicates average *not meaningful* because of large number of non-detectable values
- 3) No. indicates number of detected values

Kiln dusts, although discarded by a few plants can, in specific cases, possess characteristics that make them of interest to other uses. The most important properties are:

- ◆ low price
- ◆ the very fine particle size / high absorptive capacity
- ◆ neutralising properties due to the presence of CaCO_3 and free CaO
- ◆ enhanced levels of K_2O and SO_3
- ◆ content of hydraulically active components

These properties have lead to proposals being made for using cement kiln dust in the following applications:

- ◆ absorber material
- ◆ filler component in cement and asphalt
- ◆ neutralizing agent
- ◆ fertilizer/agricultural lime
- ◆ stabilisation of mud from oil drilling
- ◆ substitute for lime in
 - sewage sludge dewatering
 - waste stabilization
 - exhaust gas scrubbing

- ♦ glass manufacture
- ♦ rearing cattle
- ♦ production of soil replacement
- ♦ production of low grade binder
- ♦ as cat litter

Here it must be emphatically stated, that only in exceptional cases has cement kiln dust actually been used for any of the above applications in large quantities and over many years. No universally acceptable uses have yet been located for kiln dusts outside of the cement plant and their disposal problem has yet to be solved.

4.2 Methods of In-Plant Disposal of Untreated Kiln Dust

4.2.1 Addition of Dust to Cement

The most cost-effective method of using kiln dust is by incorporating it into cement. This practice was allowed early on in a few national standard specifications in European countries, which in 1989 resulted in 7 Group plants employing kiln dust in this manner. The quantity involved at single plants varied from a minimum of 0.4 wt.% to a maximum value of 8.5 wt.% of the OPC produced, with a total of 170'000 t being used in this way. In Germany kiln dust could also be added to blast furnace slag cements, where the addition resulted in improved early strength characteristics.

This use of kiln dust has since been incorporated into the European cement standard (ENV 197-1) which, as seen in Table 10, allows the addition of to 5 % of "minor additional constituents" which may include kiln dust. As can be seen this addition is allowed in all cement classes.

Table 10: ENV 197-1 Cement Types and their Compositions (wt.%)

Cement Type	Clinker (K)	B.F. Slag (S)	Pozzolana Natural (Zn)	Pozzolana Indust. (Zi)	Fly Ash Siliceous (Cs)	Fly Ash Calcareous (Cc)	Burnt Shale (B)	Limestone (L)	Silica Fume (D)	Minor Additions (F)
I	95-100	-	-	-	-	-	-	-	-	0-5
II/A	80-100	S+Z+C+B+L+D+F = 6 - 20								-
II/B	65-79	S+Z+C+B+L+D+F = 21 - 35								-
III/A	35-64	35-65	-	-	-	-	-	-	-	0-5
III/B	20-34	60-80	-	-	-	-	-	-	-	0-5
III/C	5-19	81-95	-	-	-	-	-	-	-	0-5
IV	60-90	-	0-40		-	-	-	-	0-10	0-5
V/A	40-64	18-30	18-30		-	-	-	-	-	0-5
V/B	20-39	30-50	30-50		-	-	-	-	-	0-5

- 1) Values in the table refer to cement nucleus, excluding calcium sulphate and additives
- 2) Minor additional constituents may be filler or may be one or more of the main constituents unless included as main constituents
- 3) Portion of silica dust is limited to 10% in types III/A and III/B
- 4) Portio of filler is limited to 10% in types III/A and III/B

For those countries in which the local standard specifications do not allow the addition of modest additions of kiln dust as in ENV 197-1, cement companies should, by active participation in standards committees, attempt to bring about the necessary changes in the national standard.

4.2.2 Returning to Kiln after Granulation or Compaction

Essentially this method prepares kiln dust for re-entry into the kiln by simply increasing the particle size, either by granulation (1-2 mm) or by briquetting it into long thin rods.

As far as is known the granulation method only found one practical application, on kiln 8 at Obourg, but was not needed for the larger kilns 9 and 10 as the introduction of standard specifications, which allowed the addition of dust to cement, made its use irrelevant. The layout of the kiln 8 granulator (Schugi) is shown in Figures 1 and 2.

Figure 1: Granulator for production of fine granulated powder (1 - 2 mm)

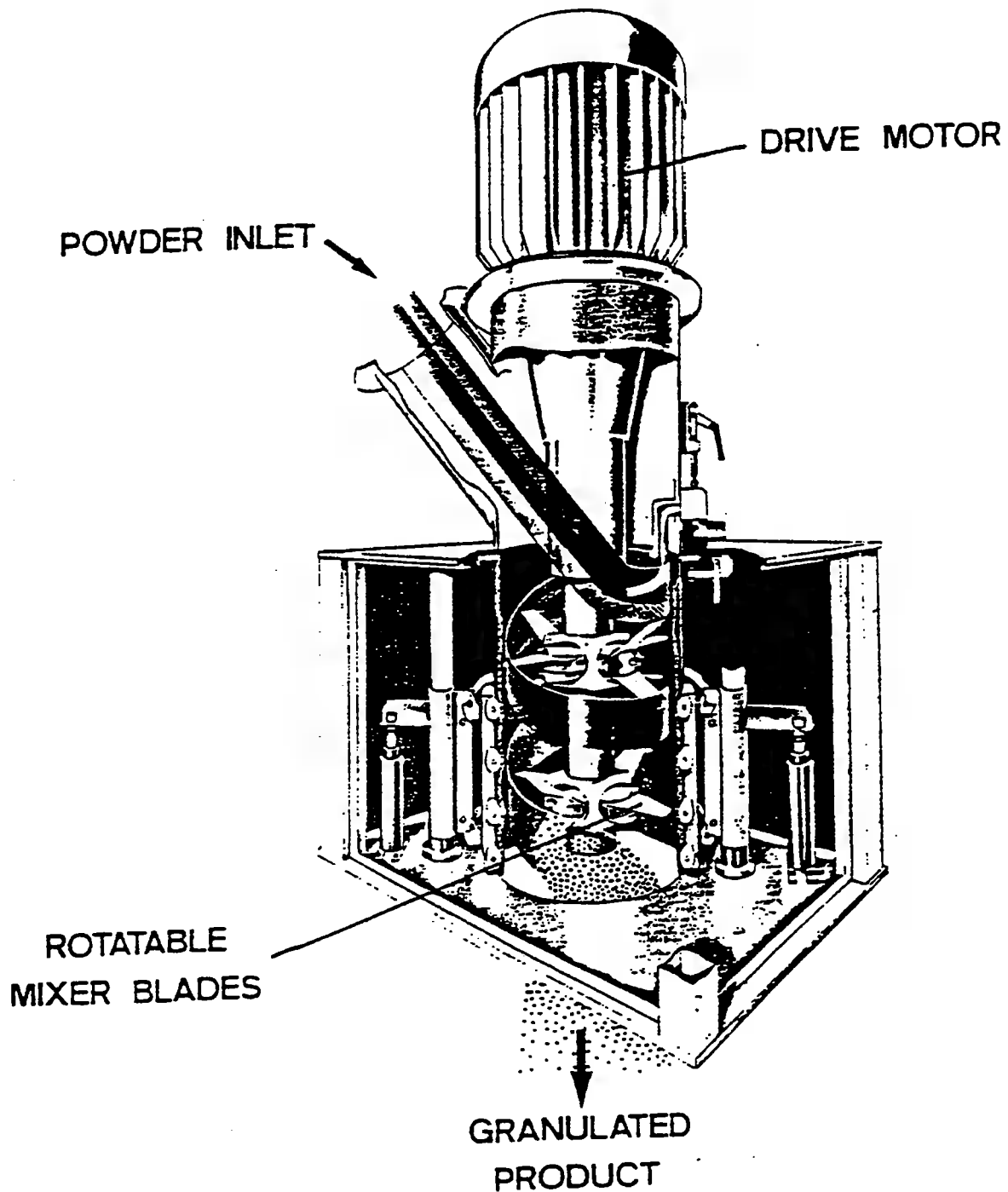
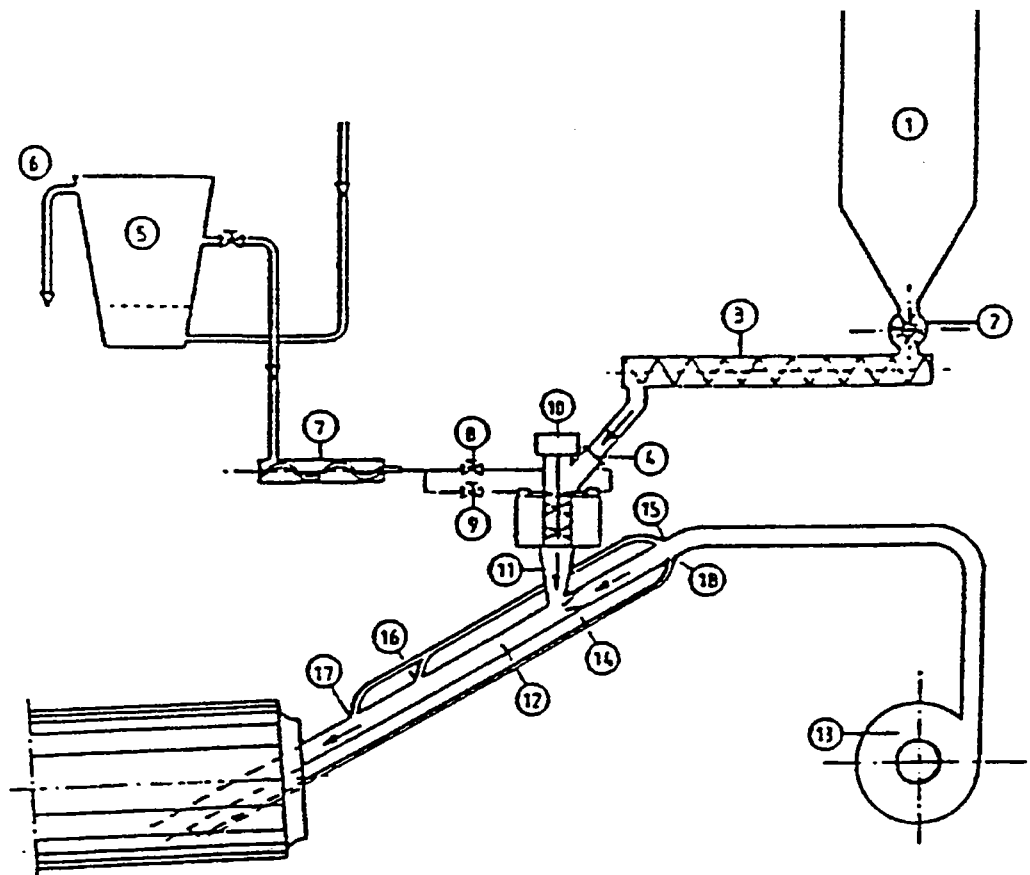


Figure 2: Dust circuit, Slurry circuit, Mixture and compressed air circuit



Dust circuit

- 1 Silo
- 2 Rotary valve
- 3 Feed screw
- 4 Stainless steel chute

Slurry circuit

- 5 Surge tank
- 6 Overflow
- 7 Slurry pump
- 8 Slurry injectors
- 9 Slurry injectors
- 10 Schugl blender

Mixture and compressed air circuit

- 11 Mixture outlet
- 12 Injection pipe
- 13 Fan
- 14 Primary injector
- 16/17 Secondary injectors
- 15/18 Branches to secondary injectors

As can be seen, the granulator consists of a vertical cylinder in which a concentric shaft is placed, rotating at a speed between 1'000 and 3'000 rpm. Attached to the shaft are several groups of knives whose angle to the shaft is continuously variable. To prevent the granules sticking permanently to the cylinder wall the latter is lined with a deformable neoprene liner which can be deformed from the outside by using pneumatically powered rollers, so causing any deposits to fall off. Kiln dust and a binding liquid are introduced into the granulator, which by the action of the rotating knives are formed into small granules, a residence time of 0.5 to 1 sec. being sufficient for granules of 0.5 mm to 1.5mm, max. 2 mm in diameter. Typically for a granulator of 10 t/h capacity only several kg of dust are present in the granulator at any one time, thus requiring an accurate and reliable dosage of both kiln dust and binder. Normally the kiln dust is itself sticky enough so that water alone can be used as granulating fluid.

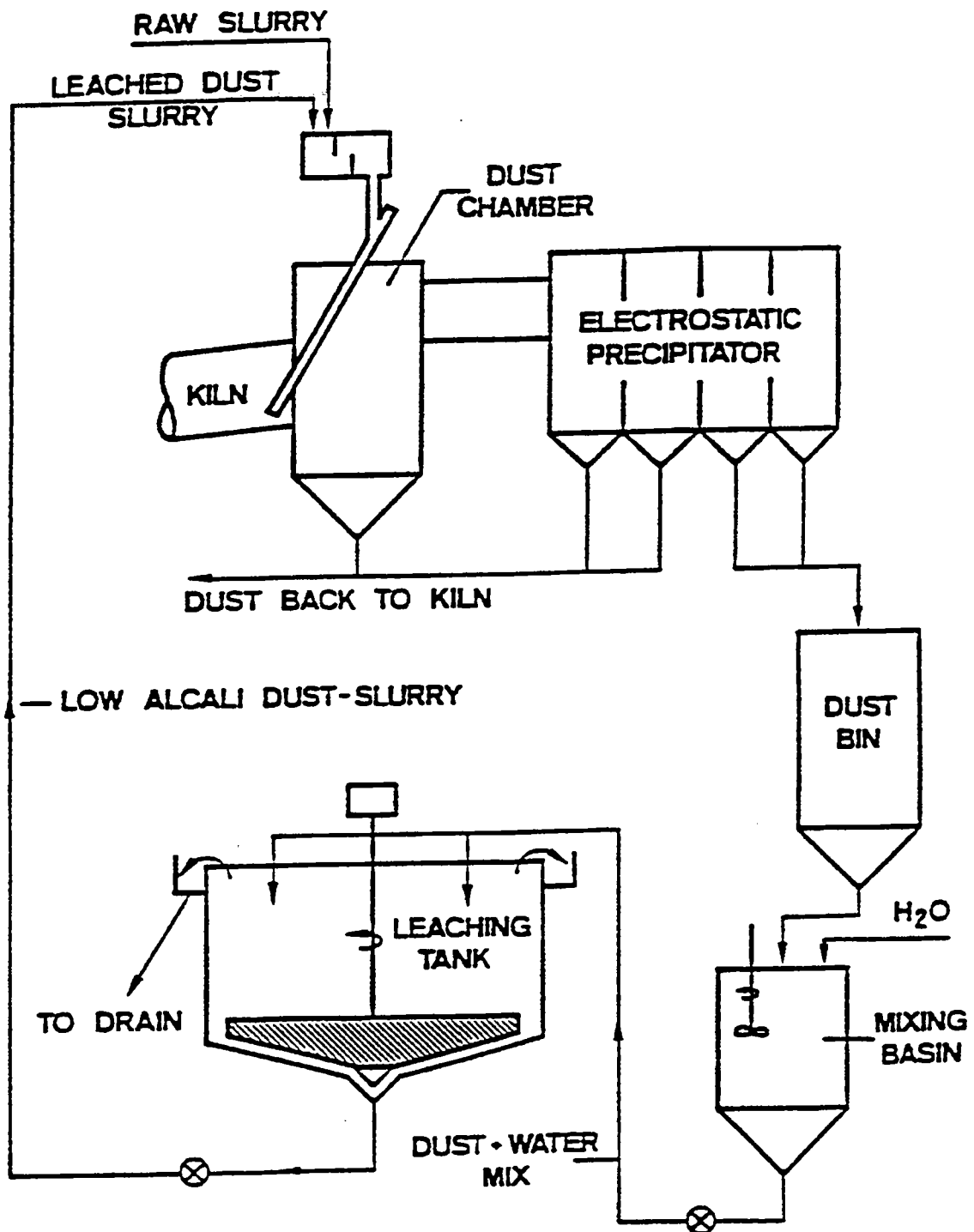
At the Obourg plant the use of equal quantities of dust and slurry allowed the whole of the dust produced in kiln 8 to be granulated and fed back to the kiln. The return of the dust in this way allowed the water content of the slurry fed to the kiln to be reduced by some 2 to 3 % and increased the quantity of the dust generated about 2 to 4 %. To prevent the granules from sticking when being fed into the kiln via the 12 m tube, they were held in suspension in a carrier gas stream. The velocity of the gas suspension was about 9 to 10 m/s and the extra quantity of air introduced some 2 %. The tube was held about 40 cm above the level of the slurry on which floated a compact bed of granules, of which about 97 % were captured by the slurry. The granulator was shut down when kiln 8 went out of production.

4.3 Methods for In-Plant Use of Kiln Dust after Removal of Alkalis

4.3.1 Removal by Simple Leaching

An early method (1963) for the treatment of wet kiln dust, so as to allow its return to kiln, is the leaching system developed and used at Holnam's Dundee plant in the USA. As far as is known this is the only leaching plant of this type in operation. Here some 350 tpd dust are collected daily from both of the plant's 1'500 tpd wet kilns. Before the installation of the bag filter in the 1990's, the coarser dust taken from the smoke chamber and the first two compartments of the electrofilter was returned to the kiln by insufflation at a rate of about 10 tph through the burner pipe. The remaining fine dust with higher levels of volatiles (from chambers 3 and 4) was processed in the leaching plant, (see Fig. 3) in which over 70 % of the alkalis were removed using quarry water. This leaching plant is still operating today but the electro filter has since been replaced by a bag type.

Figure 3: Dust Leaching System



The kiln dust is slurried batch-wise in a mixing basin using a water to dust ratio of 9:1 and then fed to the leaching tank from which the thickened slurry containing some 50 % water is then returned to the feed end of the kiln. The use of the leaching plant drops the K₂O value of the clinker from 1.1 to 0.5 % and the SO₃ from 1.0 to 0.4 %.

An important factor for the continuing operation of the leaching plant is ensuring that the effluent complies with the water pollution regulations. In the situation at Dundee the waste water disposal problem was two-fold, namely the high pH value of the leaching plant effluent and the high H₂S levels of the quarry seepage water. The two problems were reduced to one by using the quarry water for the leaching operations.

The effluent from the leaching plant has initially a pH value of 12.5 and contains S, SO₄, K, Na and Ca ions. It is neutralized by using steel mill waste pickling acid and ferrous sulphate producing CaSO₄ and Fe(OH)₂, with the H₂S being converted into insoluble sulfides. This treated effluent is then discharged into a system of three lagoons in the mined-out quarry where the solids settle out and the water is then aerated and clarified. Part of this treated water is used for clay slip preparation, the rest being discharged into the river under state regulations. As can be seen in Table 11 the operating permit of 1963 does not mention limits for the heavy toxic metals. Because of their low solubility at high pH values the concentration of the heavy toxic metals in the effluent will be anyway low.

**Table 11: National Pollutant Discharge Elimination System
(Permit No. MI. 0002020)**

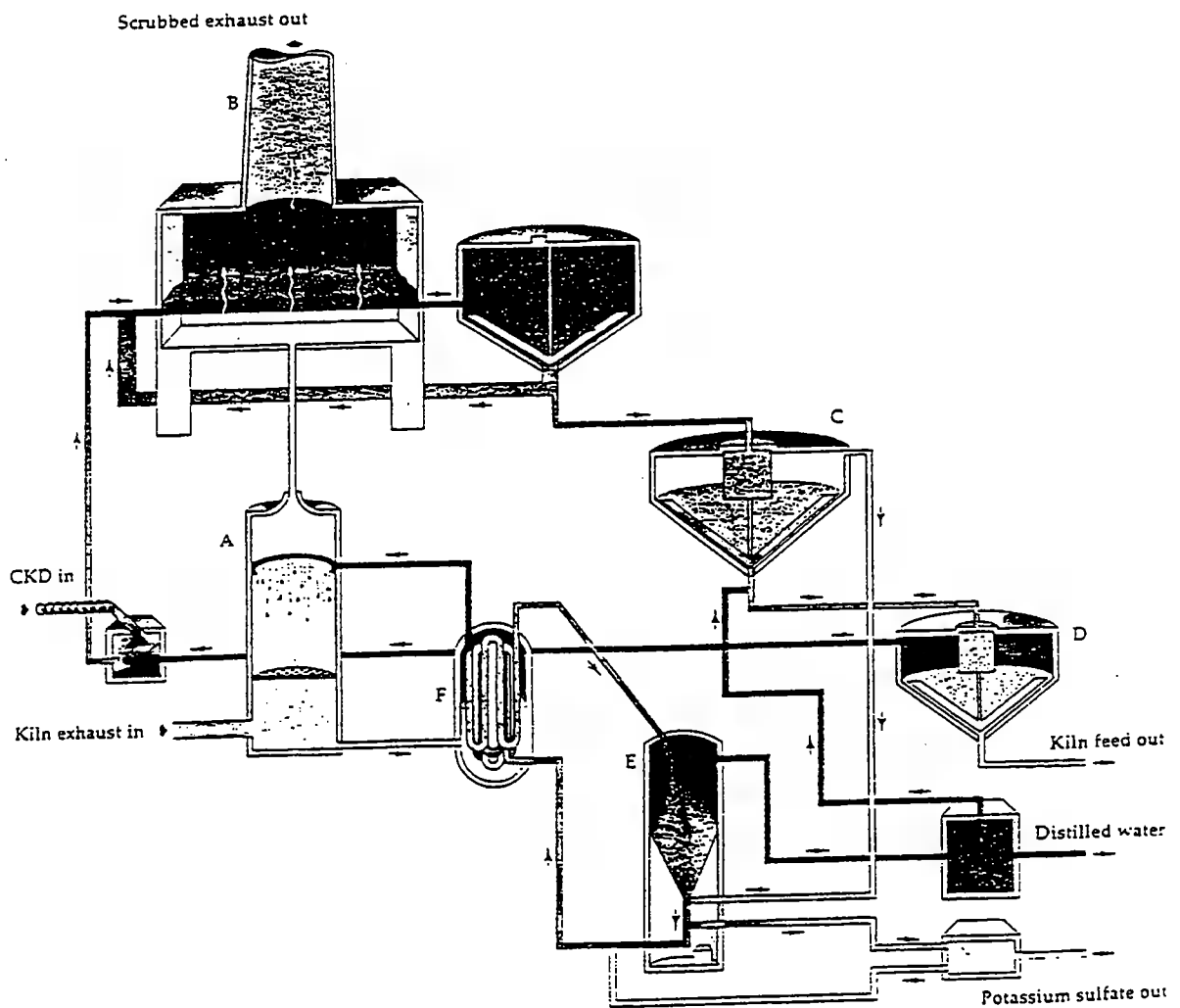
	Effluent Characteristics	Discharge Limitations	Monitoring Requirements
1.	<u>Outfall 001</u>		
	Flow	17'500 m ³ /d	Daily
	Total suspended solids	20 - 30 ppm	Daily - 24 hr. comp.
	Total dissolved solids	5'000 - 6'000 ppm	Daily - 24 hr. comp.
	Oil and grease	No visible film	Daily visual obs.
	Fecal coliform bacteria	200 / 100 m/l	Weekly grab
	Total Iron-Potassium	--	Monthly 24 hr. comp.
	Hydrogen sulfide	0.1 ppm	Weekly grab.
	pH	6.5 - 9.5	Bihourly grab
2.	<u>Outfall 001</u>		
	Flow	4'500 m ³ /d	Daily
	Total suspended solids	--	Monthly grab
	Total dissolved solids	--	Monthly grab
	Oil and grease	No visible film	Weekly visual obs.
	Temperature	--	Weekly regarding
	pH	6.5 - 9.5	Monthly grab

4.3.2 Removal by Passamaquoddy Technology Recovery Scrubber

This is essentially a modern development of the previously described leaching system and first went into operation in 1990 at the Thomaston plant in the USA. In spite of world-wide sales efforts this technology has only been installed at the above mentioned plant.

The layout of the equipment is shown in Fig. 4. An improvement over the Dundee leaching plant is that there is no discharge of alkali salt effluent into the waterways, these being converted into solid alkali sulphate/chloride to be sold as fertilizer, plus distilled water. The system also includes a scrubbing system which removes 90 % of the SO_2 from the kiln exhaust gases as well as reducing particulate emissions. It further allows the reprocessing of already dumped kiln dust.

Figure 4: Layout of the Passamaquoddy Scrubber



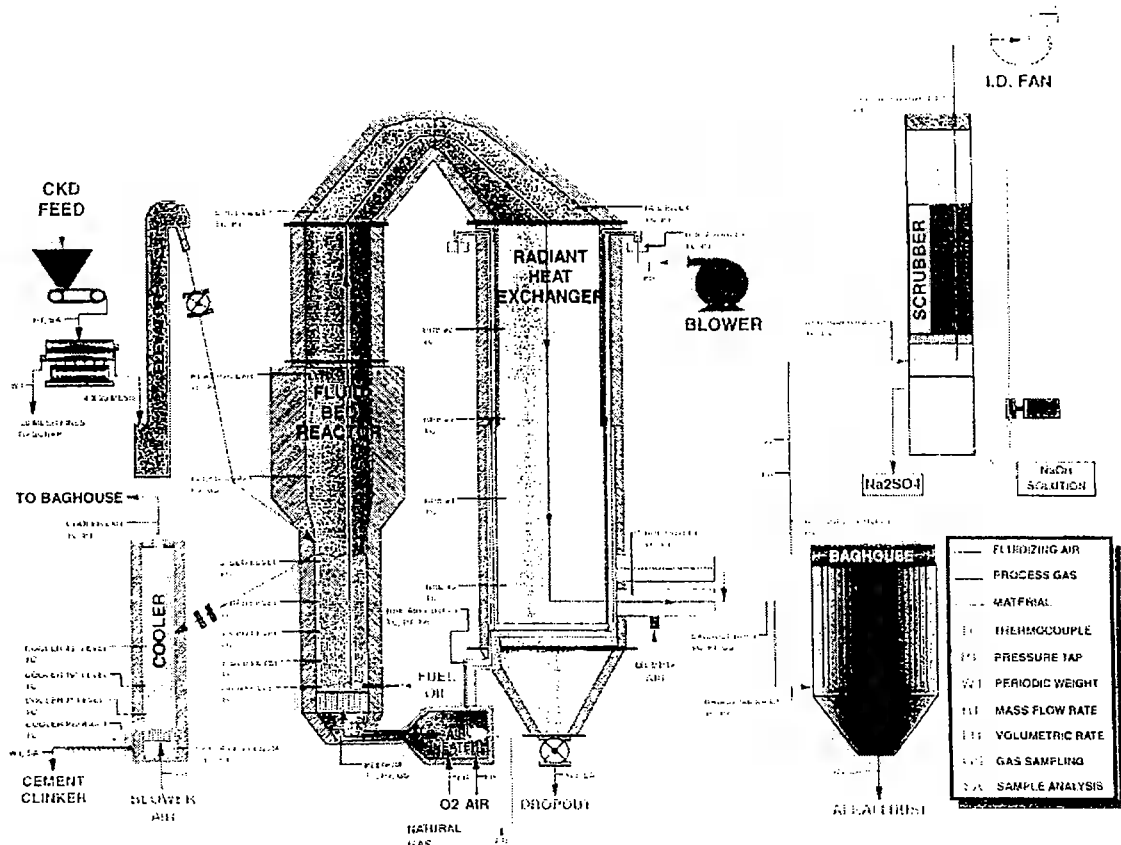
In the Passamaquoddy system kiln dust is mixed with water to form slurry just like at the Dundee leaching plant. Cooled kiln exhaust gas is bubbled through a slurry bed which reacts with lime and gypsum to form limestone and so avoids setting problems. At the same time the SO_2 and Cl in the kiln exhaust gas converts the alkalis in the slurry into soluble sulphates and chlorides. The alkaline leachate is then fed to the crystallizer, which, using waste heat from the recuperator and reduced pressure, turns it into the desired products, namely alkali salts (mainly K_2SO_4) for sale as fertiliser and distilled water. It was also said that the scrubber would be able to remove dioxins and furans and convert the heavy toxic metals into insoluble carbonates.

The reasons for the non-proliferation of this system are believed to be that the costs were very high, in the order of 30 mio USD for a 3000 tpd kiln, and that a revenue from the sale of alkali sulphate fertilizer and of distilled water was never demonstrated.

4.3.3 Removal by Auxiliary Kiln or by Fuller Fluidised Bed Reactor

In very recent times Holnam Inc., working with Fuller have carried out initial small, pilot scale trials to evaluate the possibility of producing low alkali clinker (Na_2O eqvt < 0.60%) from kiln dust using the Fuller's Fluid Bed CKD Recovery Process. Discarded dust from Holnam's Clarksville plant, both fresh and landfilled, was used for the test which demonstrated an alkali volatilisation rate < 65 % utilising a maximum permissible fluid bed operating temperature of 1310°C and oxidising conditions. The use, however, of a mildly reducing reactor atmosphere (0.8 % to 1 % CO) increased the alkali volatilisation rates to > 90 % utilising a slightly lower fluid bed temperature of 1300-1305 °C. Details of the Fuller reactor are presented in Fig. 5.

Figure 5: 18" Fluid Bed CKD Recovery System



From the results of the trials it can be said that:

- ◆ a clinker with 0.33 % free CaO was obtained after a 3 hr retention time
- ◆ the fluid bed system has a low rate of fines generation
- ◆ this fine dust, with typical composition 51.5% K₂O, 1.33% Na₂O, 33.29% SO₃ and 11.32% Cl, might be suitable as fertiliser
- ◆ the TCLP heavy metals in the dust appears to meet the limits of the RCRA leaching test.

At one plant now being built in Egypt, Polysius have foreseen the use of an auxiliary rotary kiln to concentrate the bypass dust prior to its disposal or further use.

4.4 Reported Plant External Uses of Kiln Dust

4.4.1 As Fertilizer

The features of kiln dust which make it potentially useful as a fertilizer are its potassium content, its lime content and its acid neutralizing capacity.

When compared to potassium-lime fertilizers produced by the fertilizer industry, the disadvantages of kiln dust include its variable chemical composition, its lower K_2O content, its high fineness and associated nodulizing problems.

In general a potassium fertilizer should fulfill the following requirements which may differ somewhat from country to country:

- ◆ should be in nodule form
- ◆ only slight variations in chemical composition
- ◆ should have a minimum content of soluble K_2O and CaO (In Germany the K_2O content of potassium fertilizers should be between 40 to 60 % for the chloride types and between 25 to 50 % for sulphate formulations)
- ◆ for some crops a low Cl content is required

Lime fertilizers should have a CaO content of between 40 to 90 % depending on whether they consist of calcium carbonate, burnt lime or hydrated lime.

Only two plants were known in the past to successfully market their kiln dust. These were the ENCI plant at Maastricht and Alsen-Breitenburg's Itzehoe plant, which sold their dusts as fertilizers under the "KENCICA" and "Alsen" brand names. None of these plants today sells kiln dust as fertilizer; the Itzehoe plant was closed in the early 1980's and at ENCI the kiln dust is being legally added to the cement.

With regard to their chemical compositions the dusts from these plants had quite different characteristics as shown in Table 12. The fertilizer from Alsen was of the potassium type, that from ENCI of the lime-potassium type, and as can be seen these compositions are typical of the dusts from many wet and semi-wet plants.

Table 12: Chemical Composition (wt%) of the ENCI and Itzehoe Dusts

	ENCI	ITZEHOE
L.O.I. (500°C)	1.5	1 - 2
CO_2	18	2 - 6
SiO_2	18	2 - 6
Al_2O_3	3	0.5 - 1.5
Fe_2O_3	3	0.2 - 0.9
CaO	46	5 - 15
MgO	-	0.1 - 0.3
SO_3	5	32 - 39
K_2O	5	32 - 42
Na_2O	-	2 - 3
Cl	-	1

For the successful marketing of kiln dust a very large input may not be required. ENCI for instance did not market directly under their own name but did so through a separate company having a long experience in the business of providing farmers with fertilizers. They were able to claim on the basis of crop tests that barley, turnips, potatoes and sugar beet produced the same yields as when conventional lime or potassium sulphate fertilizers were employed. It was even claimed that sugar beet contained up to 30 % more sugar when "KENCICA" was used. ENCI claimed that the CaO to K₂O ratio of 9:1 and the presence of calcium silicates made their product especially valuable as a fertilizer.

In the case of "Alsen" the company did its own marketing, an example of the promotional literature being shown (in German) in Figures 6 and 7.

Figure 6: Promotional Literature for "Alsen" Fertilizer

**Ihr Kalidünger heißt
„Alsen“ Kalifilterstaub granuliert.**

Denn damit holen Sie
mehr aus Ihrem Boden.

Mit diesen jährlichen Gaben erzielen Sie höchsten Gewinn

Empfehlenswerte Aufwandsmenge	dt/ha
Roggen, Hafer, Wintergerste, Hirsensrüchle	2,50 - 5,00
Weizen, Sommergerste	4,00 - 5,00
Kartoffeln, Haas, Mais, Wiesen, Weiden	4,00 - 7,00
Klee, Luzerne, Wurzelgemüse, Hopfen	5,00 - 8,00
Ruben, Kohlgerne	5,00 - 9,00

Preiswerteste Düngung - Vorratsdüngung

alle 2 Jahre 300 kg K ₂ O = 10 dt/ha Kalifilterstaub
oder alle 3 Jahre 400 kg K ₂ O = 13 dt/ha Kalifilterstaub

Dazu jährlich entsprechend der angebauten
Frucht Stickstoffphosphat (NP) 20-20-0.
Bei schlechten naturbedingten Bodenverhältnissen
sind höhere Gaben zu empfehlen.

Ihr Lieferant:

Neu!
Kali-Dünger

» GRANULIERT «

**Geballte Kraft
für Ihren Boden.**

ALSEN - PORTLAND-CEMENT-FABRIKEN AG - HAMBURG-ITZEHOE

Alsen Kalifilterstaub granuliert
Kalkhaltig mit optimalen Düngevorteilen

Vorteile des granulierten Kalifilterstaubs

- * große Streuleistung durch Kreiselschleuder
- * gleichmäßige Verteilung ohne Verluste durch Verstauben oder Verwehen.
- * Stoppdüngung – Vorratsdüngung
- * 100%ige Ausnutzung
- * optimale Düngung mit einem hochwertigen, neuen Kalidünger:

„Alsen“ Kalifilterstaub granuliert

Die überzeugenden Bestandteile

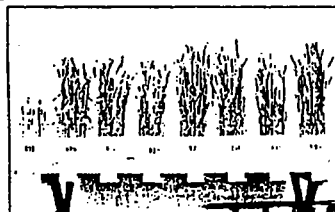
Kaliumsulfat (garantierter Mindestgehalt 30 % K_2O)
5,5 – 7,5 % Kalk (CaO)
1,5 – 2,5 % Natrium (Na)

- * Kaliumsulfat mit besonders günstigem Einfluß auf Bodenstruktur und Pflanzenverträglichkeit.
- * Kalk als wertvoller Nebenbestandteil
- * sowie wertvolle Spurenelemente

Diese Bestandteile garantieren anhaltende Düngewirkung über eine lange Spanne des Pflanzenwachstums.

„Alsen“ Kalifilterstaub in harten Vergleichsversuchen

Wie wichtig die richtige Düngemittelwahl für optimale Ernteerträge ist, beweisen immer wieder Vergleichsversuche. „Alsen“ Kalifilterstaub stellt sich diesen harten Versuchen und erzielt überzeugende Ergebnisse.



Hier der Beweis der Landwirtschaftlichen Versuchs- und Forschungsanstalt Hohenrode für Korn- und Strohertrag

Gefäß Nr.	Düngung	Korntrag g/Gefäß relativ	Strohertrag g/Gefäß relativ
311	ungedüngt	4,9 16	5,5 22
315	nur NP	25,9 87	22,5 91
Einfache Kaligabe			
319	NP + K_2 als K_2SO_4	29,9 100	24,7 100
323	NP + K_2 als KCL	25,7 86	22,4 91
327	NP + K_2 als Kalifilterstaub „Alsen“	28,7 96	26,1 106
Doppelte Kaligabe			
331	NP + K_2 als K_2SO_4	28,2 94	26,4 107
335	NP + K_2 als KCL	26,6 96	24,0 97
339	NP + K_2 als Kalifilterstaub „Alsen“	31,0 104	28,8 117

Was immer Sie anbauen – mit Kalifilterstaub granuliert ernten Sie Erfolg!



4.4.2 As Raw Material for Artificial (N-Viro) Soil

An interesting use of kiln dust, presently practised in the USA is in the production of artificial soil. The kiln dust and bypass dust from a few US plants is being sold to a specialist company - N-VIRO - which mixes the dust with partially dried sewage sludge to produce an artificial soil, marketed as N-VIRO SOIL. The kiln dust, especially bypass dust, behaves as lime and when mixed with the dried sludge, causes an increase in temperature which kills most pathogens and greatly reduces the sludge odour, all this happening within only 7 days. The production of this artificial soil is approved by the EPA as a PFRP (Process to Further Reduce Pathogens) treatment. Uses to which N-VIRO soil is put include:

- ◆ daily landfill cover material
- ◆ land and mining reclamation
- ◆ land remineralization
- ◆ highway embankment construction
- ◆ landscaping and turf material
- ◆ agricultural lime/soil conditioner

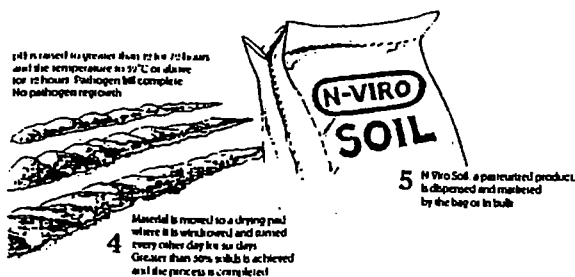
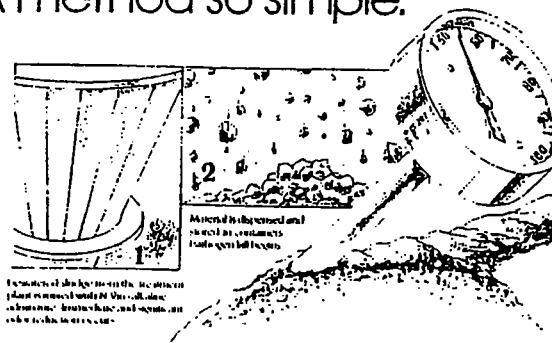
Details from N-VIRO's promotional literature are shown in Fig. 8 and the composition of the dust in Table 13.

Table 13: Chemical Composition of B

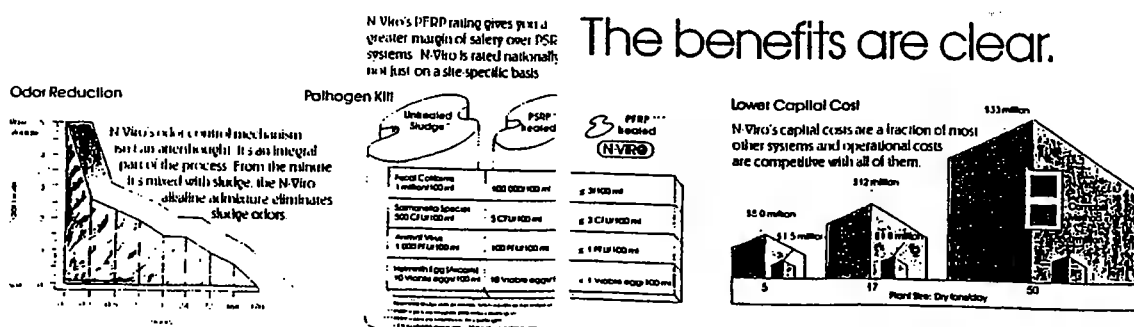
ANALYSIS	EPA-LIMIT	BYPASS DUST (%)
SiO ₂		17.55
Al ₂ O ₃		4.87
Fe ₂ O ₃		1.84
CaO		61.41
MgO		0.72
SO ₃		4.23
Na ₂ O		0.51
K ₂ O		1.53
TiO ₂		0.39
LOI		6.97
Total		100.02
E.P. TOXICITY PROCEDURE		
	Max. Limit ppm	ppm
As	5.0	0.003
Ba	100.0	2.44
Cd	1.0	0.05
Cr	5.0	0.21
Pb	5.0	0.55
Hg	0.2	< 0.001
Se	1.0	0.006
Ag	5.0	0.07
TOXICITY CHARACTERISTIC LEACHING PROCEDURE		
	Max. Limit ppm	ppm
	5.0	0.004
Ba	100.0	1.7
Cd	1.0	0.05
Cr	5.0	0.25
Pb	5.0	0.6
Hg	0.2	0.003
Se	1.0	0.002
Ag	5.0	0.04

Figure 8: Promotional Literature for "N-Viro Soil"

A method so simple.



The N-Viro Soil process converts sludge to soil in seven days without sludge odors. It is a U.S. EPA, PFRP (Process to Further Reduce Pathogens) approved process. Through this simple, five-step process, a mounting problem becomes an inexhaustible resource.



4.4.3 As Asphalt Filler

Only one plant in the "Holderbank" Group has, as far as is known, been able to sell some of its kiln dust (approx. 200 t/a) for use as a filler in asphalt, this amounting to only 10 % of the approx. 2'000 t of dust sold each year.

On the basis of laboratory trials it was ascertained that only the dust from the first chamber of the electrofilter was promising as a filler. the other dusts having the following drawbacks:

- ♦ smoke chamber: too coarse
- ♦ chambers 2, 4 and 4: too low density
too high solubility

Chamber 1 dust could be mixed with a normal filler (Vaulx) and used in the preparation of asphalt according to the Dutch "Zwacke" class. The production of "Zeer Zwacke" and "Middlesoort" classes was not possible. The proportion of natural filler that could be replaced with chamber 1 dust in the "Zwacke" grade is about 50 %. The performance of the various proportions of filler and chamber 1 dust are given in Table 14.

Table 14: Comparison of Performance of Different Proportions of Filler and Kiln Dust as Filler Component in Asphalt

Characteristics	Belgian Standards	Dutch Standard			Filler (Vaulx)	Proportion Filler: Cust (Filed 1)				
		Z.Zwakke	Zwakke	Middlesoort		20:80	30:70	40:60	50:50	60:40
Residue on:										
1 mm		0	0	0	0	0	0	0	0	0
0.09 mm		0 - 15	0 - 15	0 - 15	5 - 10	5 - 10	5 - 10	5 - 10	5 - 10	5 - 10
0.63 mm		5 - 25	5 - 25	5 - 25	13 - 19	14.5 - 20.0	14.5 - 20.0	14.5 - 20.0	14.5 - 20.0	14.5 - 20.0
Apparent density in toluene	0.5 - 0.8				0.5 - 0.6	0.43	0.45	0.43	0.46	0.48
Porosity	30 - 50	> 29	> 36	> 44	30 - 34	46.5	46.0	43.7	43.9	39.5
Sensitive to water	< 10	< 10	< 10	< 10	< 10	0	0	0	0	0
Swelling	< 3	< 3	< 3	< 3	0.35 - 1.0	3.0	2.8	2.7	2.7	2.5
L.O.I (150°C)		< 1.5	< 1.5	< 1.5	0.1 - 0.21	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Solubility in water		< 10	< 10	< 10	0.38 - 1.90	12.5	11.6	9.6	8.5	7.1
Bitumen (Getal)		28 - 30	40 - 50	54 - 60	32 - 37	58	56	55	50	44

5. DISPOSAL OF BYPASS DUST

5.1 In Plant Use

Because the original purpose of a bypass is to reduce the levels of Cl or alkalis in the kiln system, it is just not possible to return the dust so extracted to the kiln. At one Group plant (Höver) some 16 tpd of bypass dust (at times up to 30 tpd) is generated, equivalent to some 4'400 t/a. The composition of the dust is given in Tables 15 and 16. As can be seen the enrichment in Pb, Cd and Hg is high, the value for Pb being higher when tyres are being added as secondary fuel at the kiln inlet. Although it was possible in the past to dump bypass dust in the quarry, this is no longer the case and so uses have had to be found for this material.

Table 15: Bypass dust chemical composition

main components %	raw meal	clinker	bypass dust	enrichment factor raw meal bypass dust
ignition loss	35.8	0.3	6.5	
SiO ₂	13.5	21.7	12.5	
Al ₂ O ₃	3.6	6.1	2.2	
Fe ₂ O ₃	1.3	2.0	2.5	
CaO	43.2	66.5	31.0	
MgO	0.6	1.1	0.4	
SO ₃	0.6	1.0	11.0	18.3
Na ₂ O	0.3	0.3	2.6	8.6
K ₂ O	0.6	0.9	18.4	30.1
Cl	0.06	0.007	11.5	191.6

Table 16: Bypass dust chemical composition

trace elements mg/kg/10 ⁻⁴ %	raw meal	clinker (not analyzed)	bypass	enrichment factor raw meal bypass dust
Sb	2.1	--	10.0	5.0
As	10.4	--	64.0	6.1
Be	1.0	--	1.6	1.6
Pb	21.0	--	947.0 (450)*	45.0 (21)*
Cd	1.0	--	46.0	46.0
Cr	16.0	--	90.0	5.6
Co	2.0	--	11.0	5.5
Cu	5.0	--	28.0	5.6
Mo	2.0	--	6.0	3.0
Ni	12.0	--	38.0	3.2
Hg	0.05	--	2.0	40.0
Se	2.0	--	56.0	28.0
Tl	4.0	--	27.0	7.0
V	41.0	--	80.0	2.0

*without burning tyres

Several plant internal uses have been found for the bypass dust including:

- ◆ addition at raw material preparation
- ◆ feeding to the raw meal
- ◆ addition to OPC and slag cements as allowed by ENV 197-1

The bypass dust is added to the raw meal only when the Cl content in the kiln feed falls to 0.04% to 0.05 % and sufficient dust is added to give a constant level of 0.08 % Cl. This ensures a smooth bypass operation. When added to cement the quantities are limited by the requirement that the maximum Cl content should be less than 0.1 %, and is in fact held constant at 0.05 %. The quantity of dust added on a cement basis varies between 0.8 and 2.25.%. The maximum quantity of bypass dust that can be used within the plant by this method amounts to some 2'400 t/a. As an instantaneous recycling is not always possible, some dust must be temporary stored until it can be used as previously described. Other plant internal potential uses which have been evaluated but did not lead to success were in the production of:

- ◆ low quality hydraulic binders
- ◆ special binding agents for salt mining

6. DISPOSAL OF REFRACTORIES

6.1 Background

Prior to the 1980's the disposal of spent refractories invariably involved dumping the broken out material in the quarry. Thus only monetary aspects were taken into consideration and any potential burden on the environment was ignored. The introduction of strict dumping regulations has also altered this practice but in some countries an equally undesirable situation now exists. There, the same refractory materials which are continuously being worn down inside the kiln during normal operations cannot be disposed of by slow addition to the raw materials after their removal.

What quantities of spent refractories have to be disposed of? For say an average wet kiln, with a total consumption of 750 g/t basic refractories and 450 g/t of acidic materials this will mean that about 190 g/t of basic and 110 g/t of acidic refractories, i.e. 300 g/t in total actually have to be disposed of. This represents only some 0.03 % of the annual clinker production (0.019 % on a raw material basis). Assuming the spent refractories are disposed of over a period of 1 month this would mean the incorporation of 0.23 % spent refractories into the raw materials. This quantity is very small and is less than the quantity of most waste materials from other industries being disposed of in cement industry kilns.

HMC / CS is of the opinion that the plants of the "Holderbank" Group should aim at being able to dispose of all their spent refractories by incorporation into the raw materials.

6.2 Materials Involved and their Chemical Compositions

6.2.1 Materials Involved

In the widest sense the waste materials associated with cement kiln refractories must also include the packing materials in which they are delivered. This includes wooden pallets, paper and plastic packing, steel and plastic drums etc. Such materials are disposed of within the framework of a plant's general refuse concept (see Chapt. 2) and will not be further considered.

The spent refractory materials fall mainly into the following categories:

- ◆ basic bricks of the magnesia and doloma types
- ◆ high alumina bricks
- ◆ fireclay and lightweight insulating bricks
- ◆ dense refractory concrete
- ◆ insulating boards
- ◆ steel plates, steel anchors

Most is in the form of bricks.

6.2.2 Chemical Composition

The chemical compositions of typical cement kiln refractories as supplied are given in Table 17. Here it can be seen that, apart from the elevated MgO and Cr₂O₃ contents of some types, their compositions are similar to the oxide components used in clinker manufacture. During their operational lifetime the original chemical composition changes due to various reactions which include:

- ♦ reaction with non volatile CaO and SiO₂ from kiln charge
- ♦ reaction with CO₂ and SO₂ kiln atmosphere (doloma types)
- ♦ reaction with alkalis and sulphates to form Cr⁶⁺ compounds (magnesia chrome types)
- ♦ pick up of alkalis, sulphates and chlorides into open pores

Table 17: Typical Chemical Composition of Various Classes of Refractories (Unused)

Element	Magnesia Spinel	Magnesia Chrome	High Alumina	Dolomite	Fireclay	Refractory Concrete
L.o.I.	0.15	0.22	(2.7)	0.29	0.12	0.98
SiO ₂	63	2.3	11.5	0.61	55	49.8
Al ₂ O ₃	10.5	8.5	77.5	0.27	39.1	24.2
Fe ₂ O ₃	0.57	4.9	1.6	0.88	1.8	2.6
CaO	0.91	1.2	0.13	58	0.32	13.9
MgO	87	71.5	0.23	37.6	0.11	1.5
SO ₃	0.01	0.01		0.02	0.01	0.14
K ₂ O	0.02	0.02	0.32	0.02	1.1	0.94
Na ₂ O	< 0.01	< 0.01	0.02	0.01	0.12	3.7
TiO ₂	0.04	0.11	3.1	0.02	1.5	1.3
Cr ₂ O ₃	0.15	12.3				
Mn ₂ O ₃	0.01	0.08	0.01	0.08	0.02	0.05
P ₂ O ₅	0.07	0.04	2.8	0.02	0.15	0.05
Cl	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01

6.3 Regulatory Aspects / Manufacturers Safety Data Sheets

Within the European Union and the USA various regulations are now in operation which regulate the disposal of spent kiln refractories. Details have already been given in Chapt. 2.

Of importance to cement plant refractories specialists is the safety data sheets that most European refractory manufacturers are now beginning to draw up. An example of such a safety sheet, issued to comply with EU Guideline 91/155/EG, is given in Appendix I. As can be seen in page 3 of this guideline, comments are made regarding the disposal of the refractory materials (cut pieces and breakout) and also of the packing materials.

These guidelines are for consumers in general and do not take into account the cement kilns capability of disposing of its worn refractories. Normally mention is made to the presence of Cr^{6+} .

6.4 In-plant refractories disposal

In many Group plants, especially in Europe, spent refractories are cost effectively and safely disposed of via the kiln, into which they are introduced at a controlled dosage rate by:

- ◆ milling in the raw mill or by
- ◆ milling in the coal mill

In both cases the spent refractories first require to be crushed and any steel plates, shims or anchors removed by a magnet (or in some cases by hand) before grinding

The crushing process can be either carried out in:

- ◆ existing plant crushers (raw materials or clinker) or using
- ◆ a mobile crusher from an external company (disposal via coal mill)

The route via the coal mill is of special importance for the case of spent doloma refractories in wet process plants as their inclusion into the raw materials would have an adverse effect on slurry viscosity and pumpability.

In the following examples are given of several methods of in plant disposal.

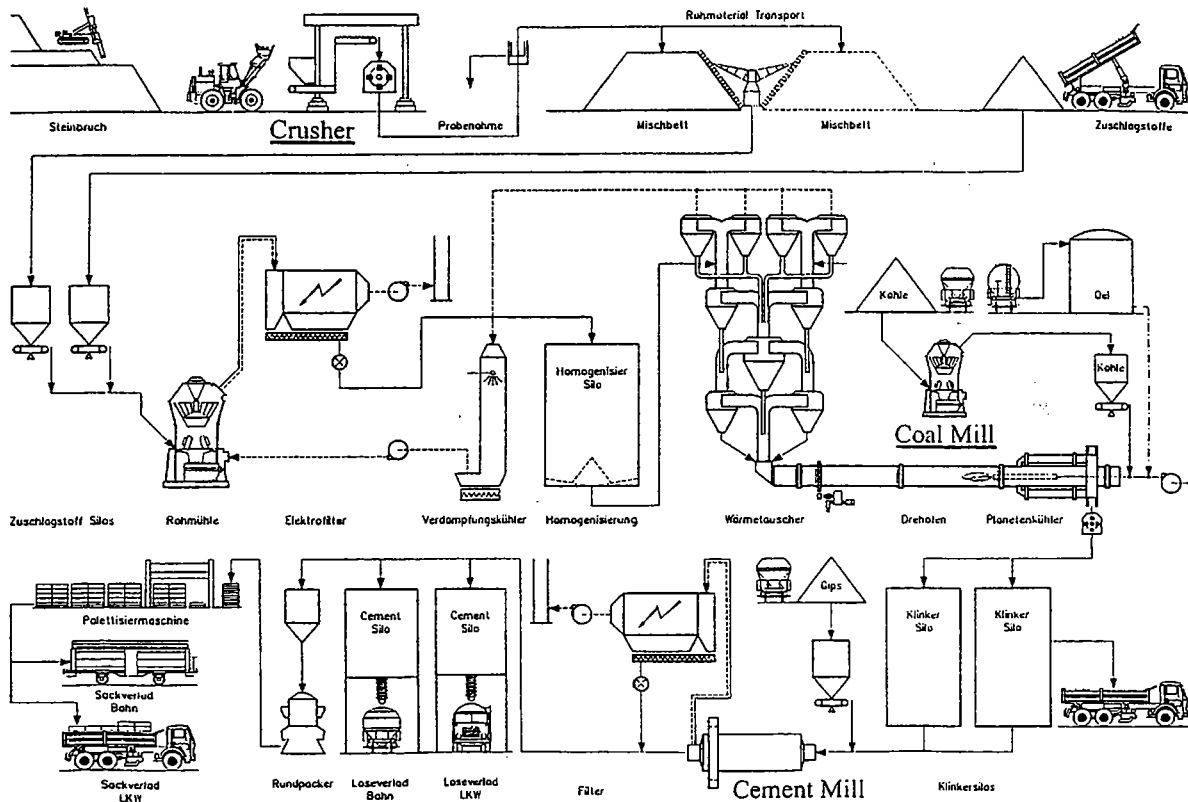
6.4.1 Plant "A"

In this semi-wet process plant fitted with a filter press, the spent bricks leave the kiln via the grate cooler and are crushed via the clinker crusher. They are then transported on a band, where a magnet removes any metal, to a small silo from which the crushed refractories are weighed into the raw feed at a slow controlled rate. The waste refractories are thus kept within the plant, require no additional handling and are effectively out of sight.

6.4.2 Plant "B"

In this large wet process plant the spent refractories are removed from the kiln via a man hole and are taken by truck to a covered storage. At regular intervals an external contractor crushes the spent material with a mobile crusher and removes the steel present. The crushed refractories are fed slowly into the coal mill and introduced into the kiln as an additional "fuel ash". It is thus homogeneously distributed.

Figure 9: In-Plant disposal of Worn Refractories



7. RECYCLING OF SPENT CEMENT KILN REFRACTORIES

The philosophy of:

- ◆ avoiding / reducing waste,
- ◆ recycling or down cycling it,
- ◆ generating energy by its disposal and
- ◆ finally disposing of the "ultimate waste"

is now becoming established in many developed countries. When applied to cement kiln refractories all these possibilities, with the exception of energy generation, are in principle thinkable.

Under the motto, "nothing will be recycled until it is economic", the recycling of spent cement kiln refractories does not appear to offer much potential. The only materials that could in theory be completely recycled are the small volumes of cuttings from unused bricks bricks and rest bricks which were never installed. Once used refractories from cement kilns are normally not suitable for recycling.

When viewed from a purely financial viewpoint low cost firebricks will never be worth recycling and only high cost qualities such as magnesia spinel might have some potential. From a technical viewpoint used cement kiln refractories are always contaminated with a host of substances which substantially lower their melting temperature and so prevent their re-use in cement kilns. At best recycling means use in a lower or non refractory context and certainly not in the cement industry.

From a practical point of view compound materials such as monolithics will probably never be able to be recycled. The recycling of dolomite qualities would necessitate the resintering of the material because of deterioration of the sinter due to hydration.

In Japan used magnesia chrome bricks from the cement and glass industries are classified as hazardous wastes and are returned to the supplier. This magnesia chrome waste is recycled as gunning mixes for application in BOF steel works.

However, even if landfilling costs were to become astronomical the fact that the possibility remains (or should remain) for a cost effective disposal via the clinkering process, means that it is very unlikely that cement industry refractories will ever need to be recycled on a regular basis.

As far as the production of cement is concerned the remnants of kiln refractories cannot be returned and recycled by the refractory manufacturer. The techniques required for this are not available and the quantities involved are small. Kiln refractories are and will stay consumable items. Only in a few developing countries are worn kiln refractories used outside of the plant as aggregate for the production of low quality refractory concrete. This form of "disposal" could not be practised in developed countries.

8. Appendixes

8.1 Appendix Ia

MATERIAL SAFETY DATA SHEET following 91/155/EEC

Last revision: September 25/95

Code: SD.304.1-0
State: Sept. 25/95
page: 1 of 4

Tradename:

PERILEX® 80 / PERILEX® 83

1 Identification of the substance/preparation and of the company/undertaking

1.1 Supplier: **REFRATECHNIK GmbH**
1.2 Address: **D-37079 Göttingen, Rudolf-Winkel-Straße 1**
1.3 Telephone: **(Germany) 0551 6941 0**
1.4 Telefax: **(Germany) 0551 6941 104**
1.5 Telex: **968 63, 968 11**
1.6 Information: **R&D-Department (0551 6941 208)**
1.7 Emergency Telephone No.: **R&D-Department (0551 6941 208)**

2 Composition/Information on ingredients

2.1 Chemical Characterisation: **Magnesia chrome brick**

CAS-No.	Chemical name	Concentr. in %	Symbol	R-Phrases
1309-48-4	Magnesia	50 - 100	n.k.	n.k.
1308-31-2	Chrome ore	2.5 - 10	n.k.	n.k.

3 Hazards Identification

As supplied the product is not dangerous. During handling (cutting, grinding, wrecking) non-siliceous dusts may be formed (see also chapter 8.). Under oxidising alkaline operating conditions the chromium³⁺ compounds may form minor amounts of chromium⁶⁺ compounds. Chromium⁶⁺ compounds are known to cause injury to the skin and respiratory tract which may lead to cancer. Chromium⁶⁺ compounds are water soluble and may lead to aquatic toxicity.

4 First Aid Measures

4.1 General Information: **none**
4.2 Inhalation: **Remove to fresh air**
4.3 Skin contact: **Wash gently with soap**
4.4 Eyes: **Flush eyes with plenty of water, seek medical care**
4.5 Ingestion: **Drink plenty of water, seek medical care**
4.6 Information for the Doctor: **none**

5 Fire-fighting Measures

5.1 Suitable Extinguishing Media: **no restrictions. As per surrounding area.**
5.2 Extinguishing Media which must not be used for Safety Reasons: **none**
5.3 Special Exposure Hazards arising from the Substance or Preparation itself, Combustion Products, Resulting Gases: **none**
5.4 Special Protective Equipment for Firefighters: **not necessary**

8.2 Appendix Ib

MATERIAL SAFETY DATA SHEET following 91/155/EEC

Last revision: September 25/95

Code: SD.304.1-0
State: Sept. 25/95
page: 2 of 4

Tradename:

PERILEX® 80 / PERILEX® 83

6 Accidental Release Measures

Avoid dry sweeping. Wet material, sweep up and bag. Minimize dust generation.

7 Handling and Storage

- 7.1 Handling: A small amount of dust may be generated during handling.
7.2 Storage: Store dry and cool away from fierce heat that may cause damage to packaging material.

8 Exposure Controls/Personal Protection

- 8.1 Engineering measures: Ensure sufficient ventilation during handling.
8.2 Specific Control Parameters:

CAS-Nr.	Substance	Type	Limit
	general limit for dust (< 5 µm)	MAK ¹⁾	6 mg/m ³
	chromium ⁶⁺ compounds	MAK ¹⁾	0,1 mg/m ³

¹⁾ Maximum concentration at working place

8.3 Personal Protective Equipments 8.3.1 General Protective and Hygienic Measures:

Keep away from food. Before breaks and at the end of work wash the hands.

- 8.3.2 Respiratory Protection: Approved dust respirator recommended
8.3.3 Hand Protection: Gloves recommended
8.3.4 Eye Protection: Approved eye protection recommended
8.3.5 Clothing: Safety boots recommended

9 Physical and Chemical Properties

- 9.1.1 Appearance: solid
9.1.2 Colour: grey-brown
9.1.3 Odour: n.a.

		Value/Range	Unit	Testing Method
9.2.1	Melting Point/Melting Range:	1980	°C	
9.2.2	Boiling Point/Boiling Range:	n.a.	°C	
9.3	Flashpoint	n.a.	°C	
9.4	Flammability (solid, gas):	not flammable		
9.5	Ignition Temperature:	n.a.	°C	
9.6	Autoflammability:	n.a.		
9.7	Explosive Properties:	not explosive		
9.8.1	Lower Explosion Limit	n.a.	Vol.-%	
9.8.2	Upper Explosion Limit	n.a.	Vol.-%	
9.9	Vapour Pressure:	n.a.	mbar	
9.10	Bulk density:	at 20 °C		
9.11.1	Solubility in Water:	at 20 °C		
9.11.2	Solubility in:	at °C		
		2.90 - 3.05	g/cm ³	
		not soluble		
		n.a.	mg/L	

8.3 Appendix Ic

MATERIAL SAFETY DATA SHEET following 91/155/EEC

Last revision: September 25/95

Code: SD.304.1-0
State: Sept. 25/95
page: 3 of 4

Tradename:

PERILEX® 80 / PERILEX® 83

9 Physical and Chemical Properties (Cont.)

9.12	pH-Value in:	at 20 °C	approx. 10
9.13	Partition Coefficient, n-Octanol/Water		n.a.
9.14	Viscosity:	at °C	n.a. log POW
9.15	Solvent Separation Test:	at °C	n.a.
9.16	Solvent Content		n.a. %
9.17	Other Data:		n.a. weight-%
			none

10 Stability and Reactivity

- 10.1 Conditions to avoid: Magnesia containing bricks can react with water to form hydrates which are non-hazardous, but destroy the bricks mechanically. Minor amounts of chromium⁶⁺ may be formed from chromium³⁺ compounds under oxidising and alkaline operating conditions.
- 10.2 Materials to avoid: Water
- 10.3 Hazardous Decomposition Products: none
- 10.4 Further Data: As supplied the product is even under elevated temperatures stable.

11 Toxicological Information

none

12 Ecological Information

- 12.1 Persistence and Degradability: persistent.
- 12.2 Mobility: none
- 12.3 Bioaccumulative Potential: none
- 12.4 Further Ecological Informations: Before undertaking the wrecking of used magnesia-chrome refractory linings, customer are advised to evaluate any changes to the product that may be induced by the introduction of substances and operating conditions not under the control of vendors. The product in the supplied or unused form can be disposed as solid non-hazardous waste according to national laws and subject to the absence of chromium⁶⁺ compounds.

13 Disposal Considerations

- 13.1 Product: Before disposing examine that amounts of chromium⁶⁺ and dispose the product according to the result of this examination.
- 13.2 Contaminated Packing Material: Combust or dispose

14 Transport Information

8.4 Appendix Ib

MATERIAL SAFETY DATA SHEET following 91/155/EEC

Last revision: September 25/95

Code: SD.304.1-0
State: Sept. 25/95
page: 3 of 4

Tradename:

PERILEX® 80 / PERILEX® 83

9 Physical and Chemical Properties (Cont.)

9.12	pH-Value in:	at 20 °C	approx. 10
9.13	Partition Coefficient, n-Octanol/Water		n.a.
9.14	Viscosity:	at °C	log POW
9.15	Solvent Separation Test:	at °C	n.a.
9.16	Solvent Content		%
9.17	Other Data:		n.a.
			weight.-%
			none

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10.2	Materials to avoid:	Water
10.3	Hazardous Decomposition Products:	none
10.4	Further Data:	As supplied the product is even under elevated temperatures stable.

11 Toxicological Information

none

12 Ecological Information

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